The Development of Electrodes for Solid Electrolytes

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FINAL REPORT - PHASE I

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DEVELOPMENT OF ELECTRODES FOR SOLID ELECTROLYTES

FINAL REPORT - PHASE I

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ABSTRACT

During this contract, the electrochemical aspects of fuel cell technology were reviewed to establish the criteria for the selection of suitable electrode materials. Based on these criteria, six materials were chosen for further study. For the hydrogen electrode, porous films of molybdenum were prepared by plasma-spraying. In contrast, for the oxygen electrode, electrodes of $NiCo_2O_4$ were prepared by chemical decomposition of the nitrates. Finally, thin films of La_2NiO_4 were deposited on a number of substrates by RF sputtering.

this contract and is discussed in Section 2 of this report. A more detailed discussion has been given in an interim report [1] and in a paper published at the World Hydrogen Conference [2]. The remainder of this contract was concerned with preliminary attempts to prepare and characterise thin films of these materials (Section 3).

The proton conductors used in the programme have been supplied from McMaster University. These include sodium yttrium silicates and sodium-pottasium β" aluminas both of which were exchanged to the hydronium form. The sodium ion conductivity of all silicates examined corresponded to data published by Nicholson et al [3], but fracture of the samples occurred upon ion exchange. The β" aluminas were fabricated under procedures outlined in patents held by the contractors [4,5] and were modified to the hydronium analog using field assisted ion exchange. Such materials were satisfactory for electrode fabrication. However, much of the work outlined in this contract was more effectively carried out using glass substrates and it is anticipated that major studies of electrodes on aluminas will take place in Phase II of the current work.

1. INTRODUCTION

A hydrogen - oxygen fuel cell requires the separation of gaseous reactants by a medium in which at least one of the reactants is mobile in ionic form. In conventional technology, the separator is a porous medium such as asbestos which is soaked in a liquid electrolyte. An alternative approach is the use of an ionically conducting solid as a separator. An example of this is the fuel cell based on zirconia where the mobile species is the oxygen ion. However the high operating temperature (>700°C) for this material causes many fabrication and lifetime problems.

It is known that hydrogen ion conductors have similar conductivities but at greatly reduced temperatures. In a quest to take advantage of this fact, a number of protonically conducting solids have been developed under joint contracts between Queen's and McMaster Universities. These ceramics are stable up to at least 300°C and it has therefore become possible to design fuel cells to operate at this temperature. However the implementation of these designs will require the selection of electrode materials which are physically and chemically compatible with the proposed system. To establish criteria for the selection of candidate materials, it is necessary to examine the thermodynamic and electrochemical aspects of fuel cell technology. This was carried out in the first few months of

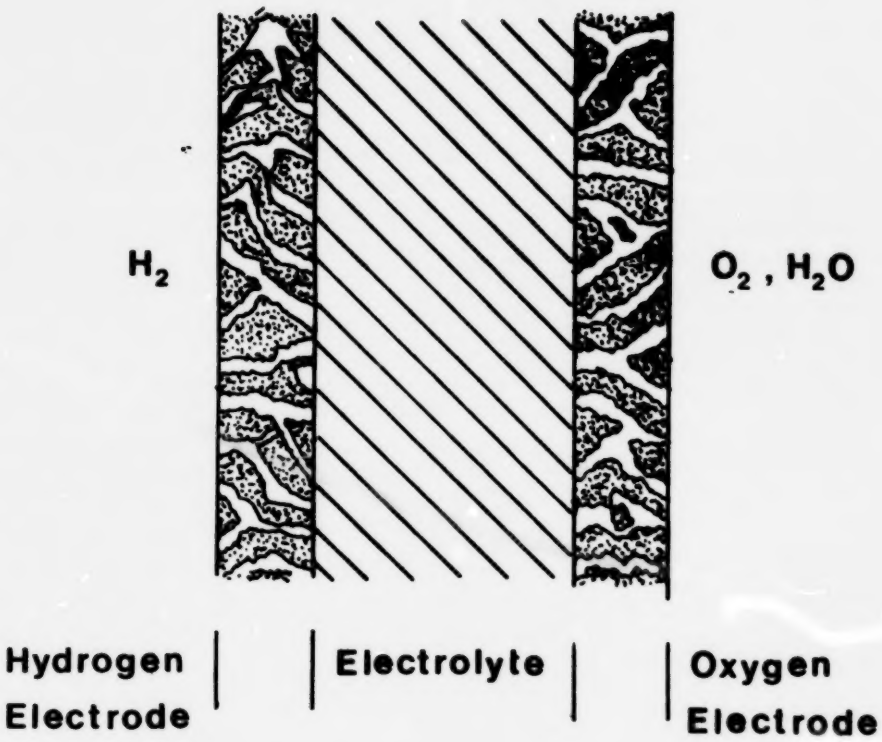


Figure 2.1 Schematic design of proposed cells.

2. OPERATING CONDITIONS

The proposed cell (Fig. 2.1) consists of two porous gas electrodes bonded to the protonically solid electrolyte. The operation of such a cell can be represented schematically by the current-voltage curves shown in Fig. 2.2. The major advantage of this system is its reversibility. Thus when hydrogen and oxygen are supplied, the cell operates as a fuel cell generating electricity at a voltage given by the dashed line (Fig. 2.2). Conversely when a voltage larger than the reversible potential, E_r, is applied to the cell, water vapour electrolysis will occur at a rate given by the solid line in Fig. 2.2. The reversible potential, E_r, is defined by the thermodynamics of the water formation/decomposition reaction and this is the starting point for the discussion of the proposed system.

Efficiency

Throughout this section, efficiencies will discussed and it is convenient here to define this term. The ideal thermal efficiency is calculated from the energy change, ΔG, according to

$$\eta_i = \Delta G/\Delta H \qquad (2.1)$$

For an operating fuel cell, it is possible to express a voltage efficiency, η_v, as a ratio of the cell voltage, E_o, for a given current load to the equilibrium

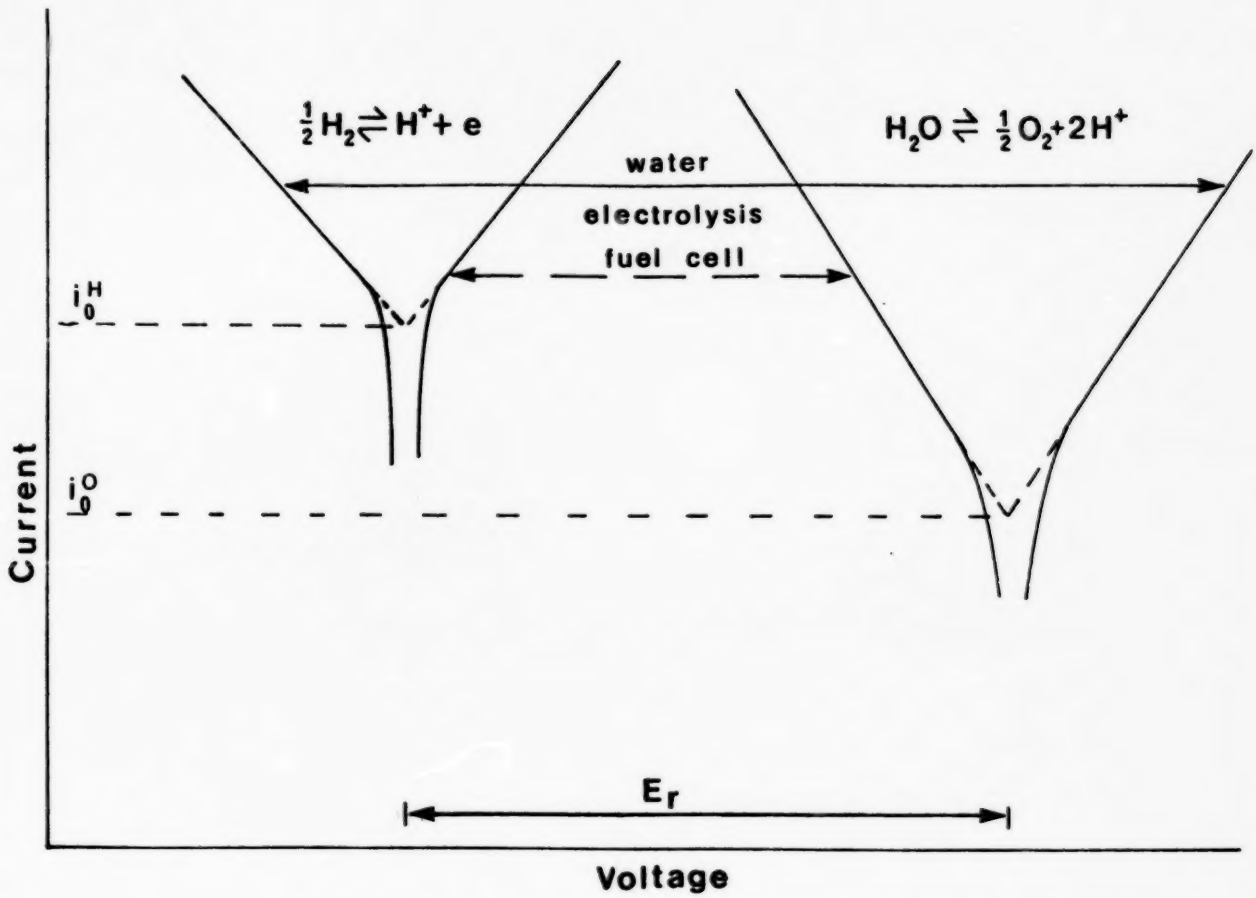


Figure 2.2 Generalised operating conditions for fuel cells and water electrolysis units

potential E_r, i.e.

$$\eta_v = E_o/E_r \qquad (2.2)$$

The energy output of an electrochemical system can also be lowered if the reactants undergo some undesired side reactions or are lost because of physical circumstances. In cases like these the desired electrochemical (Faradaic) efficiency can be less than 100% of the theoretical coulombic capacity and one can define the Faradaic efficiency as

$$\eta_f = \frac{\text{coulombs obtained}}{nF \times (\text{total moles consumed})} \qquad (2.3)$$

In the simple design proposed here, it is expected that the Faradaic efficiency will be close to 100%. The overall efficiency of an operating cell is therefore expressed as the product of the individual efficiency terms:

$$\eta_T = \eta_i \eta_v \eta_f = \frac{-nFE_o}{\Delta H} \qquad (2.4)$$

This is the efficiency used throughout this section.

2.1 Thermodynamic Considerations

The equilibrium or reversible voltage, E_r, of an electrochemial reaction is related to the free energy change by the equation:

$$\Delta G = -nFE_r \qquad (2.5)$$

The difference between the free energy change and the total energy (enthalpy) change is accounted for by a change of entropy in the process according to the relation:

$$\Delta G = \Delta H - T\Delta S \qquad (2.6)$$

which results in an approximately linear dependence of the equilibrium voltage on temperature (Fig. 2.3).

For fuel cell operation, we can calculate from equation 2.1 that an 'ideal' fuel cell operating at the equilibrium voltage of 1.12V at 300°C would have an efficiency of 89.5% (Table 2.1). This is higher than that for a cell operating at room temperature (83%) because the entropy change to produce water vapour is less than that to produce liquid water.

In terms of water electrolysis, it is convenient to define the so-called "thermo-neutral" voltage which corresponds to the enthalpy change. At this voltage, the cell would generate hydrogen and oxygen isothermally i.e. at 100% thermal efficiency. At 300°C, this voltage can be calculated as 1.25V (Table 2.1). As the enthalpy is almost temperature independent the thermo-neutral voltage varies

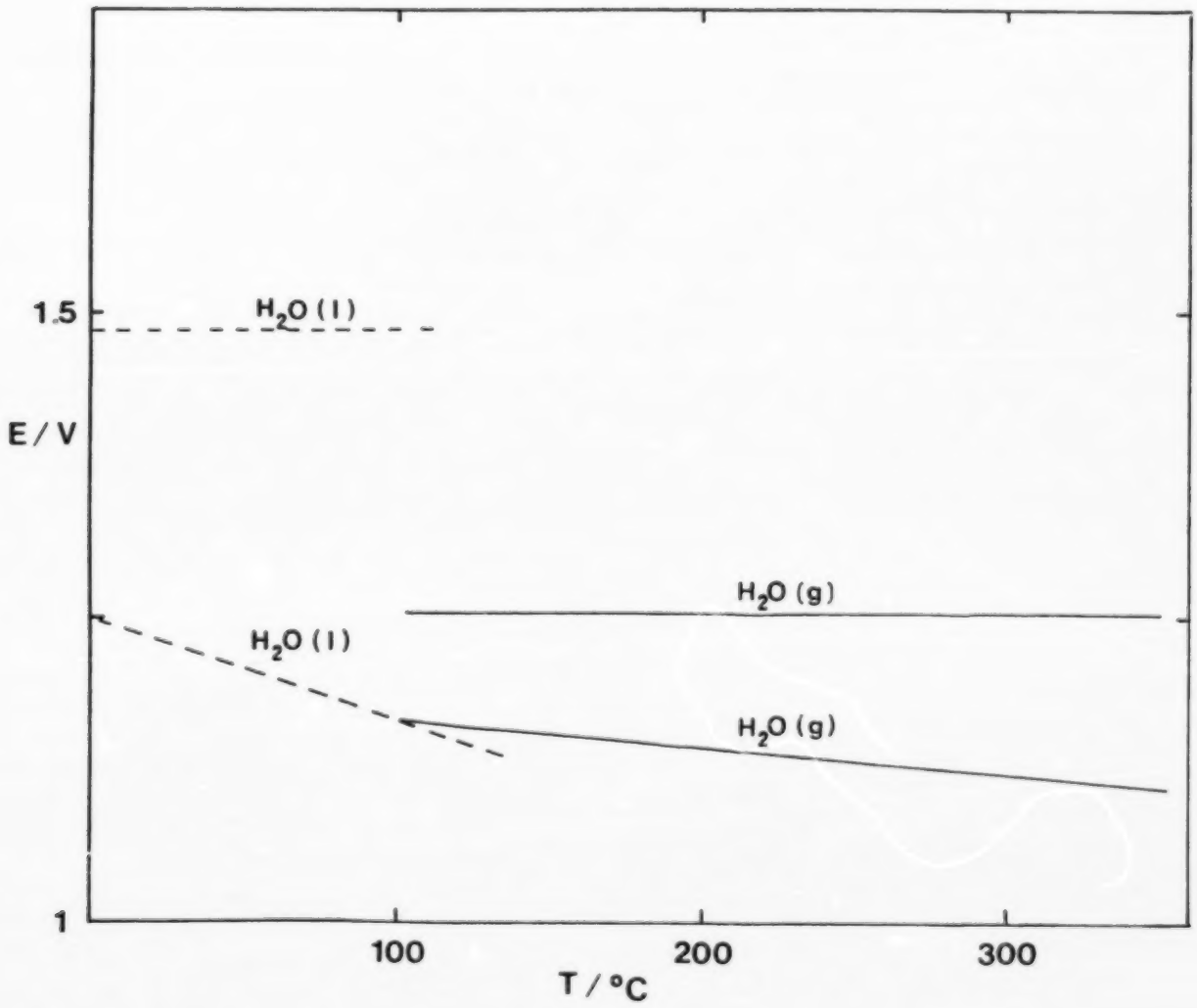


Figure 2.3 Equilibrium voltages as a function of temperature calculated from equations 2.5 and 2.6.

TABLE 2.1

Thermodynamic quantities for the reaction

$H_2(g) + 1/2O_2(g) = H_2O(*)$.

T	ΔG	ΔH	ΔS	E	η	E	water
^oK	$kJ.mol^{-1}$	$kJ.mol^{-1}$	$J.mol^{-1}K^{-1}$	V	%	V	state
298	-237.2	-285.8	-163.1	1.23	83.0	1.48	liq.
573	-216.4	-241.8	- 44.36	1.12	89.5	1.25	gas

only slightly with temperature (Fig. 2.3). Thus we can define three regions at 300°C. Below the equilibrium voltage (1.12V), the cell would operate as a fuel cell if hydrogen and oxygen are supplied. Between 1.12V and 1.25V, hydrogen is produced with an efficiency of greater than 100%. Above 1.25V, hydrogen is made at less than 100% efficiency with the liberation of waste heat.

The above analysis assumes that the reactants and products are at atmospheric pressure. However it is likely that this in general will not be the case and it will be necessary to calculate a Nernst correction to obtain the open-circuit voltage. Under the present proposals, however, it is intended, at least initially, to operate close to atmospheric pressure and this correction will be ignored in the following discussion of kinetic considerations.

2.2 Kinetic Considerations

In dealing with electrode kinetics, it is usual to employ the Butler-Volmer equation to relate the current density, i, to the operating voltage. For a simple, one-step reaction, this can be written as

$$i = i_o \left\{ \exp\left[- \frac{\alpha n F (E - E_o)}{RT} \right] - \exp\left[\frac{(1-\alpha) n F (E - E_o)}{RT} \right] \right\} \qquad (2.7)$$

where i_o is termed the exchange current density and α is the

transfer coefficient. Although this is written for a one-step reaction, similar equations can be derived when more complex reactions are considered. At high overvoltages, equation (2.7) can be reduced to the well-known Tafel equations

$$\Delta E_a = b_a \log(i_a/i_o)$$
$$\Delta E_c = b_c \log(i_c/i_o) \qquad (2.8)$$

where the Tafel constants are given by

$$b_a = \frac{2.3RT}{\alpha nF}$$
$$b_c = -\frac{2.3RT}{(1-\alpha)nF} \qquad (2.9)$$

The Tafel equation follows from the fact that the electrode reaction is an activated process and the quantity, E, is therefore referred to as the activation overvoltage. To calculate the activation overvoltage for any electrode process, it is necessary to know the values of i_o and b (and thus α) and their dependence on temperature, etc.

The exchange current density

To understand the concept of an exchange current density, it is important to realise that, at the reversible potential, an electrode is in a dynamic equilibrium, the

anodic process occuring at an equal and opposite rate to the cathodic reaction. The net flux of material and therefore the net current density is zero. However the current density in any direction (anodic or cathodic) is not equal to zero but has a value equal to the exchange current density, i_o, i.e.

$$i = \vec{i} + \overleftarrow{i} = 0 \qquad (2.10)$$

$$i_o = \vec{i} = \overleftarrow{i} \qquad (2.11)$$

Since i_o represents the current density under zero bias, it is of fundamental importance because it is related to the height of activation barrier according to an Arrhenius type equation.

$$i = A \exp \Delta G/RT \qquad (2.12)$$

The theoretical background to equation 2.12 is not clearly understood but experimentally activation energies of the order of 50-100 $kJ.mol^{-1}$ are measured.

The value of the exchange current density for any reaction depends on many variables including concentration, electrode material and electrolyte. For instance, for the hydrogen reaction on metals in aqueous acids at 25°C, it varies from $10^{-13} A.cm^{-2}$ for mercury to 10^{-2} $A.cm^{-2}$ for

platinum. For good catalytic properties, it is necessary to have as large an exchange current density as possible. This is an immediate consequence of equation 2.8 in that the activation overpotential measures the extent of interference with equilibrium at the electrode: the larger the exchange current density, the smaller is ΔE for a given external current. This represents the first criterion for the selection of an electrode material.

The transfer coefficient and the Tafel constant

For simple, one-electron electrode reactions, the transfer coefficient has been related to the symmetry of the potential barrier and is generally close to 0.5. Thus the Tafel constant for this simple process is 120mV/decade at 25°C. More complex reactions result in differing values of this slope. An example of this occurs when the reaction is sufficiently fast that the rate of the reverse reaction cannot be neglected even at the highest overpotentials employed. In this case, the reaction can be described by a Nernst equation and a slope of 60mV/decade is observed at room temperature. The transfer coefficient is generally found to be temperature independent and therefore the Tafel constant increases linearly with temperature.

The above discussion is based on concepts developed for electrochemical reactions occurring in liquid electrolytes. It is interesting to note that for charge transfer across the electrode/ solid electrolyte interface, where the charge being transferred is the mobile cation of the electrolyte, one would not expect a Tafel relationship between current and overvoltage. This is because the concentration of cations in the first layer of the electrolyte must be varied if the voltage is to be changed. Instead, the relationship for a cathodic reaction would be

$$i = C_s^{+} \exp\left(\frac{\alpha n F \Delta E}{RT}\right) \qquad (2.13)$$

where c is the concentration of cations in the first layer of the electrolyte. Equation (2.13) can be rearranged to give

$$i = i_o\left[1 + \left(\frac{C_{d\ell}\Delta E}{|q-| - \Delta\phi C_{d\ell}}\right)\right] \exp\left(\frac{\alpha n F \Delta E}{RT}\right) \qquad (2.14)$$

where $\Delta\phi$ is the potential difference between the point of zero charge and the reversible potential, E_r. Under many circumstances, the term in square brackets will be close to unity and a normal Tafel relation will be found. Equation 2.14 can be regarded as the analogue of the Frumkin correction in aqueous electrochemistry.

As the temperature is increased, the rate of the reaction increases until, at some stage, activation overpotential becomes negligble. This is certainly true both in the case of the oxygen reaction on ZrO_2 at 1000°C and also for the dissolution of sodium in β alumina at 300°C. Although the optimistic view would be that this also holds for the hydrogen reactions on H_3O β alumina at 300°C, the kinetics of electrode reactions on solid proton conductors is as yet unknown and it is therefore more realistic to assume that the Tafel relation will hold.

2.2.1 The Fuel Cell

In a fuel cell using hydrogen and oxygen, the cathodic process can be written as

$$2H^+ + \frac{1}{2}O_2 + 2e \longrightarrow H_2O \qquad (2.15)$$

and the anodic process as

$$\frac{1}{2}H_2 \longrightarrow H^+ + e \qquad (2.16)$$

which represent 2 electron and 1 electron transfer steps respectively. (These are written in this manner because the dissociations steps are expected to be fast) The operating

voltage can be written as

$$E_o = \Delta E^O + \Delta E^H$$
$$= E_r + b_c \log(i/i_o) + b_a \log(i/i_o) \quad (2.17)$$

Simulations of this equation for different values of i_o are shown in Fig. 2.4. Although in practice the exchange current densities will be unequal, they have been set equal to each other in these simulations for convenience. This probably represents a worst case situation. Using equation 2.4, it can be shown that an overall efficiency of over 60% can only be achieved if the exchange current density is greater than $10^{-2} A.cm^{-2}$. This is to be compared to conventional fuel cells which operate at an efficiency of 54%. Under these conditions, the current output would 0.1 $A.cm^{-2}$ at an operating voltage of 0.78V. It should be noted that ohmic losses have not been taken into account.

2.2.2 Water Vapour Electrolysis

Similarly, for water vapour electrolysis, we can write for the cathodic process

$$H^+ + e \longrightarrow \frac{1}{2} H_2 \quad (2.18)$$

and for the anodic process

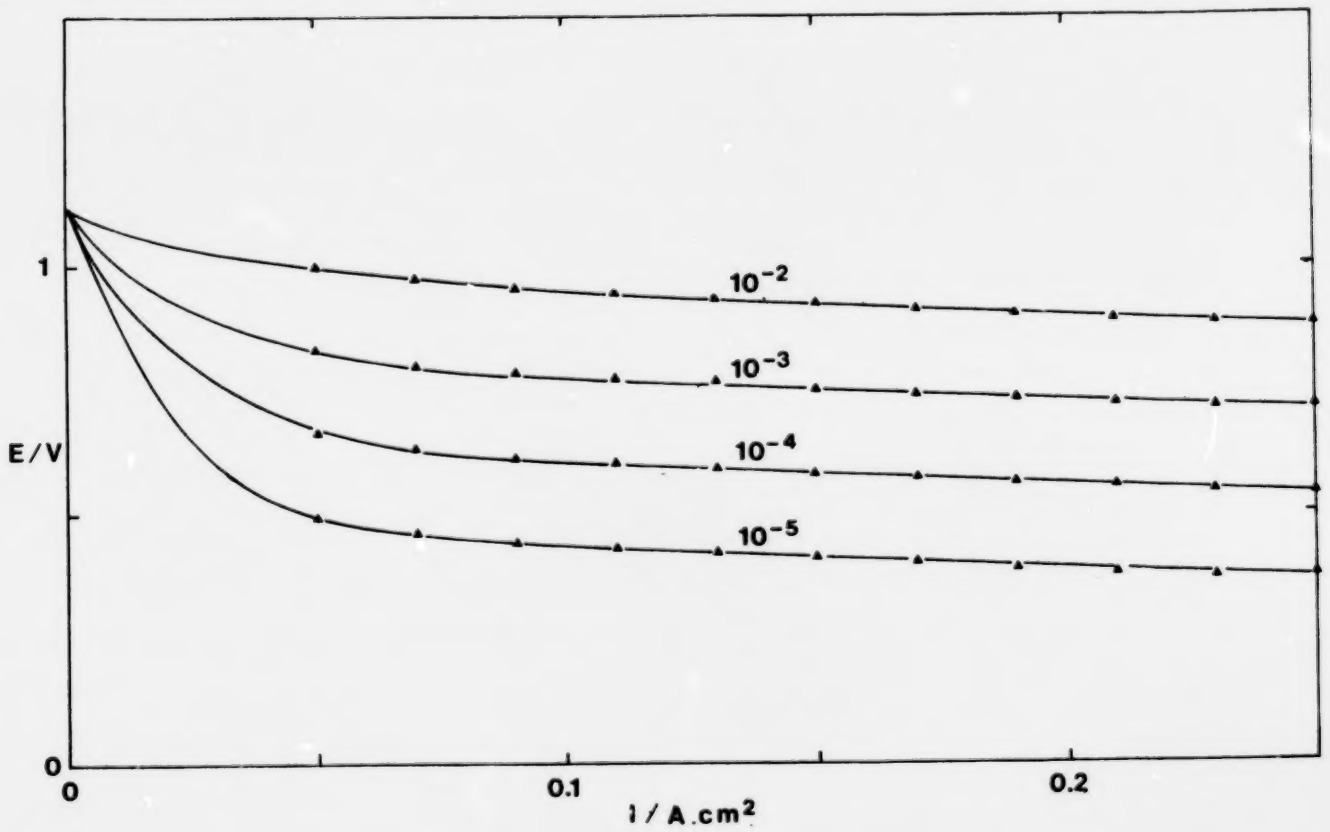


Figure 2.4 Simulated Performance for a fuel cell operating at 300°C.

(b_a=227mV/dec.; b_c=113mV/dec.)

$$H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e \qquad (2.19)$$

and thus the operating voltage is given by

$$E_o = E_r - b_a \log(i/i_o) + b_c \log(i/i_o) \qquad (2.20)$$

Again the simulations (Fig. 2.5) show a strong dependence on i_o. However, comparison of these simulations with the test data of the Noranda advanced alkaline water electrolysis unit shows that this design can be competitive if an exchange current density of $10^{-2} A.cm^{-2}$ can be achieved. Noranda have proposed an operating current density of $0.1\ A.cm^{-2}$. At this current level, the proposed design would have an operating voltage 0.16V (ca.10%) less than that of the Noranda cell representing a significant reduction in capital cost.

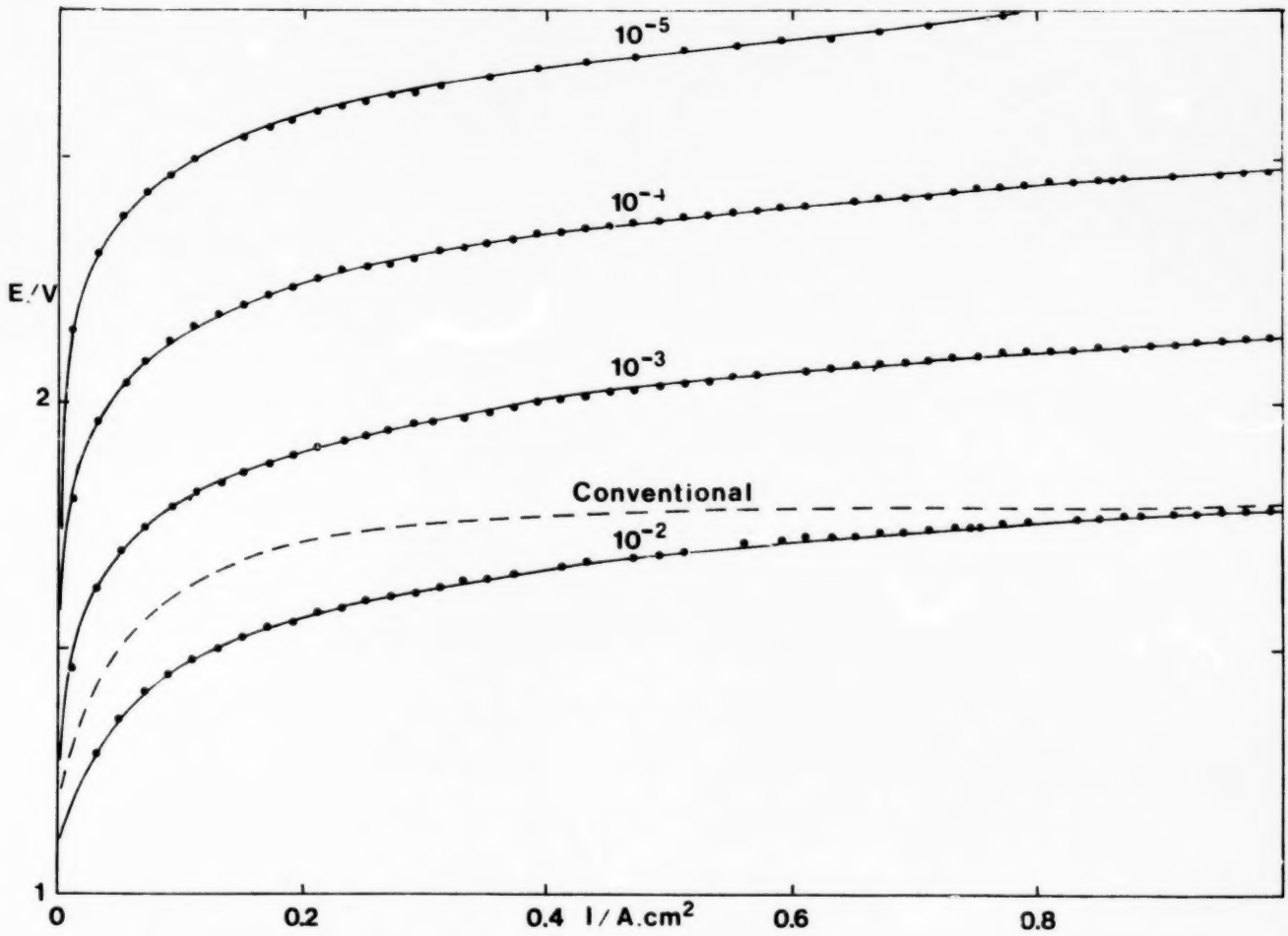


Figure 2.5 Simulated performance of a water electrolysis unit at 300°C.

(b_a=57mV/dec.; b_c=113mV/dec.)

2.3 Ohmic losses

Two sources of ohmic loss can be determined. These can be connected with the resistances of the electrode and electrolyte. At this stage of development, the primary cause of ohmic loss will probably be the electrolyte resistance which is proportional to the conductivity of the material. The resistance factor (ohm.cm^2) can be defined as

$$R = 1/\sigma \qquad (2.21)$$

In conventional water electrolysis units, R has a value of around 0.7 ohm.cm^2 which, for a 0.1 mm thick electrolyte, corresponds to a conductivity of 0.14 ohm^{-1}cm^{-1}. This is a very high value for a protonically conducting solid. However, if we compare the performance of a conventional unit with the proposed design, it can be seen that to achieve similar performance at low current densities (0.1 A.cm^2), an extra ohmic loss of 160 mV can be afforded. This would correspond to an electrolyte conductivity 0.05 ohm^{-1}cm^{-1} which seems possible to achieve.

The resistance of the electrode is more difficult to discuss as it depends on the specific design as well as the material to be used which is not known at present. In general, however, it is necessary to solve the Laplace equation for the potential distribution at the electrode/electrolyte interface. This has been carried out for a wire screen electrode and it has been shown that the

contact resistance problem is comparatively more important for thin cells or large wire spacing. This suggests that any film electrode should be as continuous as possible. Thus there is an optimum between porosity and resistance of the electrode. In terms of materials, the hydrogen electrode is likely to be a metallic conductor - either a pure metal or alloy - whose conductivity is high. The oxygen electrode, however, will probably be a complex oxide which will likely to be a semiconductor. Care must therefore be taken that the conductivity is sufficiently high.

Finally it should be noted that, as the cell operates at high temperature, it may be necessary to have the heat generated by ohmic loss to maintain the temperature of the cell.

3. MATERIAL SELECTION AND CHARACTERISATION

In the previous section, the electrochemical aspects of cell operation were discussed and, in particular, it was shown that the exchange current density was a crucial parameter in the selection of candidate materials in that it determines the catalytic activity of the electrode. In fuel cell technology, it is well known that platinum is the ideal catalyst for both the hydrogen and oxygen electrodes. However it is expensive and alternative materials must be sought. The catalytic activity of these alternative materials must compared to that of platinum under the same conditions. Thus we have carried out a number of experiments to prepare platinum films on hydronium β alumina and, for comparison purposes, these will be discussed at the end of this section.

In Section 2, it was shown that that the porosity played a conflicting role in that it not only affects the gaseous diffusion but also the electrode resistance. These requirements led to the suggestion that two types of preparation techniques should be explored. These are sputtering or plasma-spraying and chemical deposition. In the following sections, therefore, possible electrode materials will be discussed and their preparation technique indicated.

Platinum electrode preparation

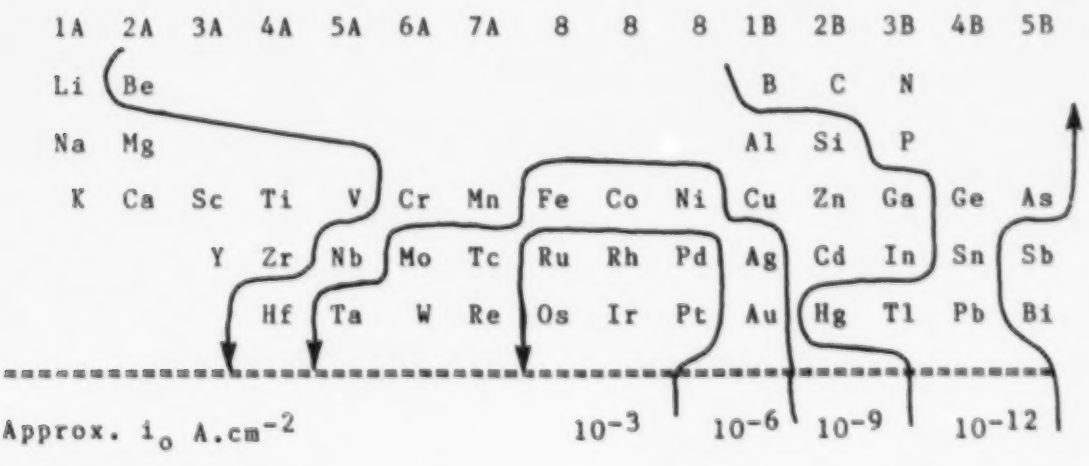
Platinum is notoriously difficult to sputter and liquid deposition techniques have been investigated. Using a platinum based paint known as liquid bright platinum, initial results suggested that it was difficult to obtain low resistance films with a single application. In contrast, electrodes prepared with a platinum paste were only poorly adherent to β alumina. However, after a careful study, it was found possible to obtain low resistance films by the successive application of very thin coats of liquid bright platinum. These have been used successfully in cells operating in the water electrolysis mode. A further difficulty arose in that it was difficult to control the porosity, in some cases the electrode was completely non-porous. Based on the observation that porous platinum electrodes on the hydrogen side improved with use, it was found that curing in hydrogen vastly improved the quality of the electrode. Moreover the films can be prepared as a single thick coat and become porous by the evaporation of the organic solvents which seems to be promoted by the presence of hydrogen. Work is continuing to characterise these layers for use as a standard for the selection of alternative materials.

3.1 The Hydrogen Electrode

The values of the exchange current density for the hydrogen reaction on a number of metals can be related to their position in the periodic table (Table 3.1). It may be seen that platinum and the transition metals near to it have reasonably high exchange current densities. As stated previously for successful operation at 300°C, an exchange current density of at least 10^{-2}A.cm^{-2} is required. Assuming an activation energy of 50 kJ.mol^{-1} - a typical value - one can calculate that, at room temperature, i_o should be in the range of 10^{-6}-10^{-7}A.cm^{-2}. For the pure metals, nickel and

Table 3.1

HYDROGEN EXCHANGE CURRENT DENSITIES RELATED TO THE PERIODIC TABLE


1A 2A 3A 4A 5A 6A 7A 8 8 8 1B 2B 3B 4B 5B
Li Be B C N
Na Mg Al Si P
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As
Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb
Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi
Approx. i_o A.cm^{-2}
10^{-3}
10^{-6}
10^{-9}
10^{-12}

molybdenum are two commonly occurring metals which have exchange current densities of this order. Nickel, however, can not be sputtered and seeems less interesting at this stage. In contrast, preliminary experiments have shown that it is relatively easy to sputter thin films of molybdenum onto Na β" alumina. The dark gray films produced are around 10 μm thick and have sheet resistances of the order of 10 ohms. Interestingly we have also been able to prepare films by the more commercially-viable technique of plasma-spraying. These are somewhat thicker (20-30 μm) but have very low resistance. However the adherence of the film to the electrolyte surface varied according to the electrolyte source. As the poor adherence seemed to be associated with the formation of a gold-coloured, interfacial layer which looked like a molybdenum bronze (H_xMoO_y), it was felt that the problem may be associated with moisture uptake by the electrolyte. This would obviously be a significant problem using hydronium β alumina but plasma-sprayed molybdenum remains worthy of further study. The techniques of sputtering and plasma-spraying may also be useful in preparing alloy systems such as $LaNi_5$ which has been shown to have long term stability and cycle life in the nickel/hydrogen battery with an alkaline electrolyte. This alloy forms a hydride under operation which could act as a storage medium. However this may cause mechanical stability

problems. In conclusion, therefore, the most promising candidate to replace platinum as the hydrogen electrode seems to be plasma-sprayed molybdenum.

3.2 The Oxygen Electrode

In a previous report, we isolated three materials as potential candidates for use as an oxygen electrode in a fuel cell. The first, La_2NiO_4, is well known in conventional water electrolysis where it has been prepared by plasma-spraying followed by a subsequent heat treatment. We have attempted to prepare thin films on a variety of substrates by R.F. sputtering. In contrast, thin films of the other two potential catalysts, $NiCo_2O_4$ and RuO_2, have been prepared by chemical decomposition. Our results will be discussed in detail in this section.

3.2.1 La_2NiO_4

A target for sputtering was prepared by pressing a stoichiometric mixture of La_2O_3 and NiO powders. This was used to prepare thin films on a variety of substrates (β-alumina, glass, NaCl, quartz and silicon). The sputtering parameters are summarised in Table 3.2.

Examination under a transmission electron microscope showed that the films were polycrystalline with a preferred orientation after annealing. Rutherford backscattering experiments showed that the films were

TABLE 3.2 Sputtering Parameters for La_2NiO_4.

Ambient Atmosphere:	100% O_2
Sputtering Pressure:	6 mtorr
RF Power:	110 W
Self-bias Voltage:	220 V
Substrate Temperature:	415°C
Sputtering Duration:	5 hours

homogeneous but that they were lanthanum deficient. This lanthanum deficiency is attributed to the differences in the sputtering yield rates of the two oxides. It has therefore been decided to enrich the starting target in La_2O_3 (10% excess).

3.2.2 $NiCo_2O_4$

Thin films of this material have been prepared by painting of the substrates (glass and β alumina) with a solution of the nitrates. After decomposition at 300°C, a black, amorphous film is produced on the surface. Initial electrical characterisation suggests that this material has a high conductivity (of the order of 100-200 ohm^{-1} cm^{-1}) and a low activation energy (0.01 eV). This combined with the fact that this material seems stable in steam at least up to 100°C makes this material worthy of further study. Preliminary testing in a fuel cell suggests that it will also act as a catalyst

3.2.3 RuO_2

In a similar manner to $NiCo_2O_4$, films of this material have been produced by thermal decomposition of the chloro-hydrate, $RuCl_2.xH_2O$. The film is black and crystalline although the x-ray powder diffraction pattern could not be indexed.

SECTION 4. SUMMARY AND CONCLUSIONS

In this year we have:

1) achieved a substantial understanding of the operation of vapour phase electrolyser and fuel cells.
2) identified two promising candidates (Pt and Mo) for the hydrogen electrode.
3) identified three candidates for oxygen electrodes.
4) In the case of Pt, the discovery of the benefits of hydrogen curing of the electrodes allows reproducible low conductivity films to be prepared in a single application. This would have significant commercial use.
5) In the case of Mo, we have developed the use of plasma sprayed coatings. These coatings have been applied by a commercial company - Jaycoat Ltd, Hickson Ave, Kingston, and by the Industrial Materials Research Institute, Boucherville, Que (Dr. Serge Dallaire). This method of coating is of industrial significance.
6) The fabrication of porous Ni-Co oxides by a simple paint formulation appears to form the basis of an excellent oxygen electrode.
7) The sputtering of stoichiometric lanthanum nickelate and the evaluation of its electrical properties has not been carried out previously.

8) In the course of measuring the electrical properties of the films we have set up a four probe Van der Pauw method for measurement of sheet resistance.

9) We have evaluated silicate based proton conductors, but currently have had little success with full ion exchange.

As noted earlier, the preliminary evaluation of the electrical and structural properties of the films has been effectively carried out by deposition on glass. The anticipated mechanical adhesion to ceramics is expected to be considerably higher. Reproducible samples of hydronium β"alumina are now available, and the future work will apply the results of films on glass to the ceramic.

SECTION 5. ACKNOWLEDGEMENTS

Thanks are due to personnel in the laboratory who have contributed to the work of this contract. These include Lois Devlin for general film preparation and laboratory services, Dr.S.B.Krupanidhi for thin film fabrication, and a number of persons who have contributed as part of the junior technician position - Hughes Le Parneaux, Dave Barr and Saulius Fidleris.

SECTION 6. REFERENCES

1. M.F.Bell and M.Sayer "Electrode Material Selection for Fuel Cells and Water Vapour Electrolysis Units" Interim Report- March 1984- present contract

2. M.F.Bell, M.Sayer, P.S.Nicholson and K.Yamashita "Low Temperature Vapour Phase Electrolysis using "alumina.

Hydrogen Energy Progress V, 571-580 (1984)

3. P.S.Nicholson and A.Pekarsky, Mat. Res. Bull. 15, 1517-1524 (1980)

4. P.S.Nicholson, M.Nagai, K.Yamashita, M.F.Bell M.Sayer and D.S.Smith.
The Preparation of a Precursor Solid for the Manufaacture of a Ceramic Hydrogen Ion Conductor
Canadian Patent Application -June 1983

5. P.S.Nicholson,M.F.Bell, M.Sayer and K.Yamashita
Method of Converting a Precursor Ceramic Solid into a Solid Ceramic Hydronium Conductor
Canadian Patent Application - Filed December 1983